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HIGH VOLTAGE BREAKDOWN
OF TITANIA IN VACUO

by

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A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

DEPARTMENT OF ELECTRICAL ENGINEERING

EDMONTON, ALBERTA

DECEMBER 1965

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ABSTRACT

The electrical breakdown of titania in a vacuum is investigated experimentally using static electric fields. Current and temperature variations at different applied voltages are examined. It is found that thermal instability occurs at voltages above a critical value. This leads to sufficiently high temperatures to cause the reduction of the titania sample. It reduces into a lower order semi-conducting material that carries the breakdown current.

The breakdown of titania and a vacuum gap in series is also investigated. Evidence gathered from temperature, current, and field emission readings suggests that, at high voltages, part of the voltage originally across the vacuum gap appears across the titania. The voltage redistribution is due to a change in the amount of charge at the surface of the titania. This change is caused by field emission. When the voltage across the sample reaches a large enough value, thermal instability occurs leading to the reduction of titania and breakdown. Supporting evidence for this theory is obtained from measurements of the mechanical force across the vacuum gap. The mechanical force measurements give the voltage at the surface of the titania for any applied voltage up to breakdown. This gives the change in voltage distribution between electrodes.

ACKNOWLEDGEMENTS

The work described in this thesis was carried out at the Department of Electrical Engineering, University of Alberta, under the supervision of Dr. C. Englefield, to whom the author is deeply indebted for his advice and assistance.

To Mrs. V. Harwood and Dr. G. Walker, sincere appreciation is extended for their help and suggestions. Acknowledgement is gratefully given to the graduate students for their helpful information. To Mr. E. Buck and the machine shop, and to Mr. N. Burtch, Mr. A. Simonson, and the rest of the technical staff, the author is also indebted.

The author is further indebted to the National Research Council and the University of Alberta for financial assistance.

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HIGH VOLTAGE BREAKDOWN OF TITANIA IN VACUO

1. INTRODUCTION

1.1 Titania

Titania is a ceramic material consisting mainly of titanium dioxide with various additives for binding and to help improve stability. Titanium dioxide alone tends to be reduced in an atmosphere with a deficiency of oxygen. The Ti^{4+} reduces to Ti^{3+} and this material is an n- type semiconductor. X-ray studies have shown that the rutile structure is maintained by titanium dioxide even for a weight loss as great as two percent (composition $TiO_{1.99}$). When the weight loss is somewhat greater, the lower oxides Ti_3O_5 or Ti_2O_3 form as a separate phase.

The properties of titania that make it a useful electrical material are its high dielectric constant (about 93) and low loss tangent (about .0003). These factors make it very useful as a loading material for microwave slow wave structures and cavities.

1.2 Surface breakdown of titania

Interest in the surface breakdown of titania began when failures occured during work on dielectric loaded periodic structures at Queen Mary College, University of London. After breakdown, the titania discs that were used as loading elements

had radial tracks of dark material on their surface. In addition there was a light brown discoloration on the interior metal walls and on the surface of the discs.

Initial experimentation (5) showed that a thin coating of glaze caused an improvement in breakdown strength. This glaze was a green resistor enamel consisting mainly of lead borate.

Investigations were then begun at the University of London and continued at the University of British Columbia by R. Hayes (2) to obtain information about the breakdown process and to determine the properties of the glaze that were responsible for the improvement in breakdown strength. Tests were made to determine the thermal stability of titania in a vacuum and it was found that it reduced to a dark semiconducting material at temperatures above 350° C.

The surface resistivity and secondary emission characteristics of the titania ceramic and of the ceramic coated with the glaze were obtained. As a result of these tests it was concluded that changes in these two properties were not responsible for the improvement in surface breakdown strength.

To obtain more information, a study was made of surface breakdown in a vacuum due to static and dynamic fields. Plain titania was shown to suffer permanent damage in the form of breakdown tracks at the instant sparking occured. These were

thought to have been formed by the local heating associated with the electrical discharge. Once formed they destroyed the insulating properties of the ceramic since they consisted of a semiconducting material. The application of the glaze coating appeared to form a protective layer that prevented the formation of the semiconducting oxides when random sparking, caused by surface contamination, occurred.

In the majority of cases surface breakdown patterns originated at points on the metal-ceramic interface. Inspection of the contact area usually revealed that the metal and ceramic did not fit exactly at these points. It was concluded that breakdown was initiated by field emission in the gaps formed by an improper metal-ceramic contact. Attempts to eliminate this by silver plating the ceramic at the cathode were successful at d-c. Silvering the contact edge at microwave frequencies however, did not result in any improvement.

To overcome this problem, S. Chute (1) deposited by evaporation a thin film of aluminum on the edge of the ceramic disc. This film substantially improved the surface breakdown strength at microwave frequencies. Increasing the film thickness provided further improvement.

1.3. Object of present work

Most of the investigations (1-5) that have been made to date have dealt with the surface breakdown of titania. This

type of breakdown was of interest because it was the principle type of breakdown that had occurred to titania discs used as waveguide loading elements.

If titania is used as a microwave window, however, the type of breakdown that is expected is punch-through breakdown. This thesis is concerned with failure due to this type of breakdown. Static electric fields are used since they permit a much more detailed picture of the pre-breakdown and breakdown phenomena than dynamic fields.

Two types of breakdown are considered:

(i) breakdown of titania

(ii) breakdown of titania and a vacuum gap in series.

In both series of tests, current and temperature readings are made at various applied voltages. In addition to this, the mechanical force on the electrodes due to the electric field in the vacuum gap is measured. From this force measurement, the field strength in the gap may be obtained. Since the voltage drop across the vacuum gap can be calculated from the field strength in the gap, the voltage drop across the titania sample may also be obtained.

2. INSULATORS UNDER HIGH VOLTAGE

2.1 Pre-breakdown Currents

When a low d-c voltage is applied to an insulator, three components of current flow.(7) These are:

(a) geometrical capacitance current

(b) absorption current

(c) conduction current

The geometrical capacitance current of an insulator is its charging current. It is an exponential function of time with a time constant dependent on the resistance of the power supply (about 2.5 M-ohms for the supply used in the investigation) and on the capacitance of the insulator (about 40 pica-farads for the titania sample). This gives a time constant of about 10^{-4} seconds for the capacitance current of the titania which makes it negligible after less than a second.

The current component resulting from absorption within imperfect dielectrics is caused by a slow somewhat viscous movement of ions and molecules under the action of the electric field. The current observed due to this absorption effect represents stored energy which may be removed by shorting the dielectric for a period at least as long as the field was applied.

There is also a frequency dependent loss associated

with this storage of energy. In the case of zero frequency (d-c) this loss is insignificant but at higher frequencies the energy loss depends on the rate of change of field strength.

Empirically, the absorption current component can usually be expressed as a function of voltage change $\triangle V$ and time 't' by equation 2.1.2.

$$I_a = \triangle V \, A \, t^{-n} \qquad 2.1.2$$

where 'A' and 'n' are constants with 'n' ordinarily ranging from zero to one.

The last of these three components of current, the conduction current, is the primary cause of energy losses that occur in an insulator due to the application of a static field. Both the electrons in the conduction band and the vacant states or holes left in the valence band will contribute to the electrical conductivity. This gives rise to conductance that is proportional to the number of electrons per unit volume 'n_e' in the conduction band and also to the number of holes per unit volume 'n_h' in the valence band. Thus the conductance may be expressed as

$$s = |e| \, (n_e U_e + n_h U_h) \qquad 2.1.3$$

In this equation, 'e' is the charge on an electron, and U_e' and 'U_h' are the mobilities of the electrons and holes respectively. Since, for proprietary reasons, nothing is known about the additives used in making the particular type

of titania ceramic used in the experiments, the assumption is made that the titania is pure (intrinsic). Thus the temperature dependence of 'n_e' and 'n_h' will be the same as for the corresponding entities in a semiconductor. The temperature dependence of 'n_e' may then be written (20)

$$n_e = A\ T^{3/2} \exp\left[(E_m - E_g)/kT\right] \qquad 2.1.4$$

Also, the temperature dependence of 'n_h' is (20)

$$n_h = B\ T^{3/2} \exp\left[-E_m/kT\right] \qquad 2.1.5$$

In these equations 'A' and 'B' are constants, 'T' is the temperature in degrees Kelvin, 'E_m' is the 'Fermi Level' ($E_m >> kT$), 'E_g' is the energy gap between the valence band and conductance band (3.0 to 3.8 ev for titania (15)), and 'k' is Boltzmann's constant (all energies are measured relative to the bottom of the conductance band).

Since the holes are caused by electrons that have moved into the conduction band, the number of holes must be equal to the number of electrons. That is

$$n_e = n_h \qquad 2.1.6$$

If 'n_e' and 'n_h' are multiplied together and the square root of the resulting expression is taken, the equation for 'n_e' and 'n_h' becomes

$$n_e = n_h = \sqrt{AB}\ T^{3/2} \exp\left(-E_g/2kT\right) \qquad 2.1.7$$

The conductance may then be written

$$s = |e|\ (U_e + U_h)\ \sqrt{AB}\ T^{3/2} \exp\ (-E_g/2kT) \qquad 2.1.8$$

Assuming that the temperature dependence of the mobilities is insignificant in the temperature range of interest, this becomes

$$s = DT^{3/2} \exp\ (-E_g/2kT) \qquad 2.1.9$$

where 'D' is a constant

The energy gap 'E_g' is constant and so the equation may be written in terms of another constant 'a'

$$s = DT^{3/2} \exp\ (-a/T) \qquad 2.1.10$$

For pure titania 'a' should be about 2×10^4 °K. The conductivity 's' at room temperature has been measured by the author and found to be about 10^{-12} ohm-cm for an applied voltage of about 200 volts.

Since the samples of titania used in the experiments have grain boundaries and impurities which affect the conductivity and as the mobilities are not independent of temperature, this equation will probably be true only over a limited temperature range.

2.2 Breakdown strength

Experimentally, insulators (dielectrics) usually break down in one of three ways.(10) The type of breakdown that occurs depends on the manner in which the voltage is applied. If the voltage is applied quickly, either intrinsic or avalanche breakdown occurs. These are both thought to be

electronic in origin. Some authors (8, 15) have classified them together theorizing that avalanche is intrinsic breakdown occurring in thin samples. The other type of breakdown, thermal breakdown, occurs in most insulators when a voltage is applied slowly. It is caused by local overheating arising from electrical conduction.

The idea of breakdown strength as a material property is complicated by the wide variations resulting from testing procedures. It is also difficult to produce absolutely uniform fields and this affects the results.

(a) Intrinsic breakdown

The main distinguishing features of intrinsic breakdown are:

(i) It occurs at any temperature.

(ii) Breakdown strength is relatively independent of the size and shape of the sample and of the material or configuration of the electrodes at a given temperature.

(iii) Breakdown occurs in times of micro-seconds or less.

Failure is thought to occur when a localized voltage gradient reaches some value corresponding to the intrinsic breakdown strength. At this value, electrons in the structure gain enough energy to free other electrons by collision. This process continues until enough electrons are freed to

form an electron avalanche (which corresponds to breakdown).

(b) Avalanche breakdown

Avalanche breakdown has some of the features of intrinsic breakdown.

Its distinguishing features are:

(i) It occurs in thin slabs of very low electrical conductivity and very high breakdown strength. Breakdown strength increases as the thickness decreases.

(ii) If the voltage is applied slowly, the pre-breakdown current is very erratic. If a sudden over-voltage is applied, the time for breakdown is subject to considerable statistical variation.

Avalanche breakdown is thought to occur when a single electron (or a few electrons) can cause an avalanche of electrons of sufficient size to destroy the insulating properties of the sample. The noisy pre-breakdown currents are explained in this theory by avalanches that fail to reach a critical size. The gradient is great enough for intrinsic breakdown but the path is not long enough for a destructive avalanche to occur. This also accounts for the increase of breakdown strength with decrease in thickness.

(c) Thermal breakdown

Some characteristics of thermal breakdown are:

(i) It occurs at high temperatures.

(ii) The breakdown field strength depends on the size

and shape of the sample and also on the geometry and thermal properties of the electrodes.

(iii) The time to breakdown depends on the applied voltage and is at least milliseconds or longer.

(iv) With alternating fields, the breakdown strength is usually lower than the d-c value because of frequency dependent losses.

Thermal breakdown occurs along paths where the natural non-homogeneity of the material causes a greater than normal conductivity. Electrical energy losses raise the temperature and further increase the conductivity. This causes local instability which leads to high temperatures and fusion or vaporization of the material along the path.

The energy transferred to the material along such a path due to an applied field E may be written

$$B = s E^2 \qquad 2.2.1$$

where 's' is the electrical conductivity. This energy will raise the temperature of the material to an extent dependent upon thermal losses. Assuming that thermal conductivity is the only significant loss process, the energy balance equation may be written

$$C \frac{\partial T}{\partial t} - \operatorname{div} (K \operatorname{grad} T) = s E^2 \qquad 2.2.2$$

where 'C' is the specific heat, 'K' is the thermal conductivity, and 'T' is the temperature in degrees Kelvin. Since 'K' and 's'

are always temperature dependent (especially 's') and 's' may also depend on the field strength, even approximate analytic solutions are possible only for the simplest boundary conditions.

This equation has been solved by Copple et al$^{(14)}$ for the simple one-dimensional case. The sample considered was an infinite slab as shown in figure 2.2.1.

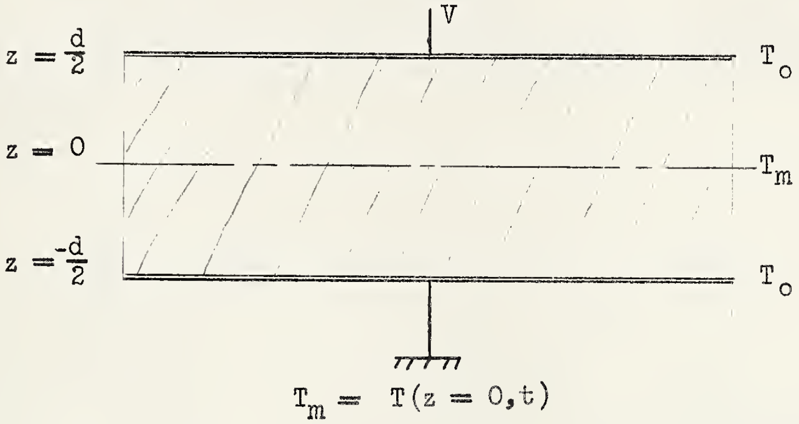

Figure 2.2.1 Infinite Slab

The surfaces were both held at some ambient temperature 'T_o' and 'T_m' was the temperature at the hottest spot in the sample (along the plane $z = o$).

This gave an equilibrium equation of the form

$$C \frac{\partial T}{\partial t} - K \frac{\partial^2 T}{\partial z^2} = sE^2 \qquad 2.2.3$$

This equation was obtained by assuming that 'C' and 'K' are invarient. The temperature dependence of 's' was taken to be

$$s = s_o \exp (bT) \qquad 2.2.4$$

It was chosen by Copple et al because experimental measurements had indicated that some insulators followed this

type of relationship approximately over the temperature range of interest (between room temperature and the material's breakdown temperature).

Substituting into equation 2.2.3 yielded

$$C \frac{\partial T}{\partial t} - K \frac{\partial^2 T}{\partial z^2} = s_o E^2 \exp(bT) \qquad 2.2.5$$

The solution of this equation(14) for various values of 'E' gave the following set of curves for the hottest spot in the sample.

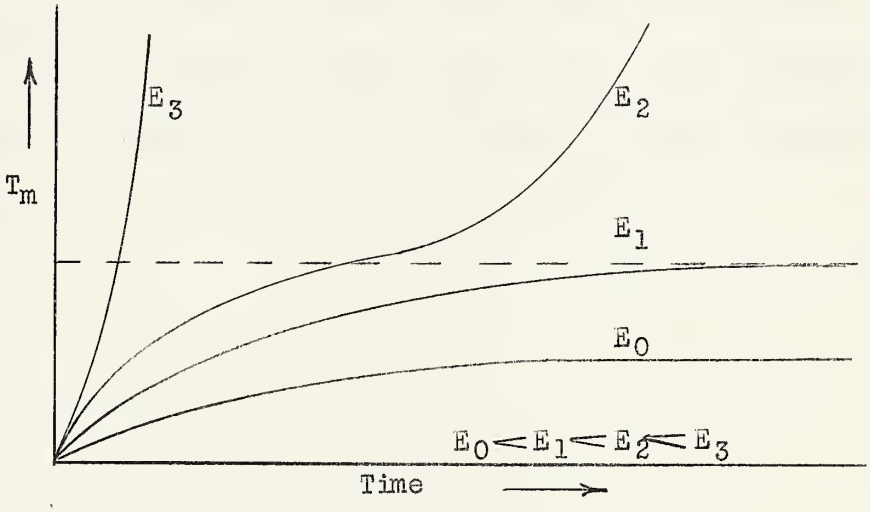

Figure 2.2.2 Temperature versus time for an Infinite Slab

As can be seen from figure 2.2.2, when the field strength is above some critical value, the temperature will rise until melting or chemical decomposition yields a high enough conductivity for electrical breakdown. This critical value of field strength is sometimes called the thermal breakdown strength of

a material. However, an insulator may be used at fields above its critical field strength for short periods of time.

Thermal runaway occurs as a result of the exponential increase of conductivity with temperature. Since the values of 's_o' and 'b' in equation 2.2.4 may be chosen so that equation 2.2.4 approximately follows equation 2.1.10 between room temperature and 700°K (appendix I), thermal runaway should occur in the titania (700°K is the temperature at which the titania is expected to reduce to a semiconducting material in a vacuum(2)). If thermal runaway does occur, a set of curves like those in figure 2.2.2 will be obtained for various applied voltages.

3. BREAKDOWN OF TITANIA IN A VACUUM DUE TO STATIC ELECTRIC FIELDS

3.1 Vacuum system and high voltage supply

(a) Vacuum system

A block diagram of the vacuum system is given in figure 3.1.1. Pumping was performed by a 2-inch mercury diffusion pump backed by a rotary pump. A liquid nitrogen cold trap was used in conjunction with the diffusion pump to prevent contamination of the working chamber by mercury. With this system, the ultimate pressure obtained was 10^{-6} mm Hg.

The working chamber was a pyrex glass cross with a four inch inner diameter. Viton seals were used on all flanges and connections in the high vacuum part of the system.

Pressure measurements were made using a Pirani gauge in the 1 mm to 10^{-3} mm Hg range and a cold-cathode Penning gauge in the 10^{-3} mm Hg to 10^{-6} mm Hg range.

(b) High Voltage source

The high voltage d-c source was a conventional half-wave rectified supply delivering a continuously variable output voltage up to 50 kv. Several features were included in the unit for safety.

An electronically controlled relay system opened the high voltage transformer primary when an excessive current

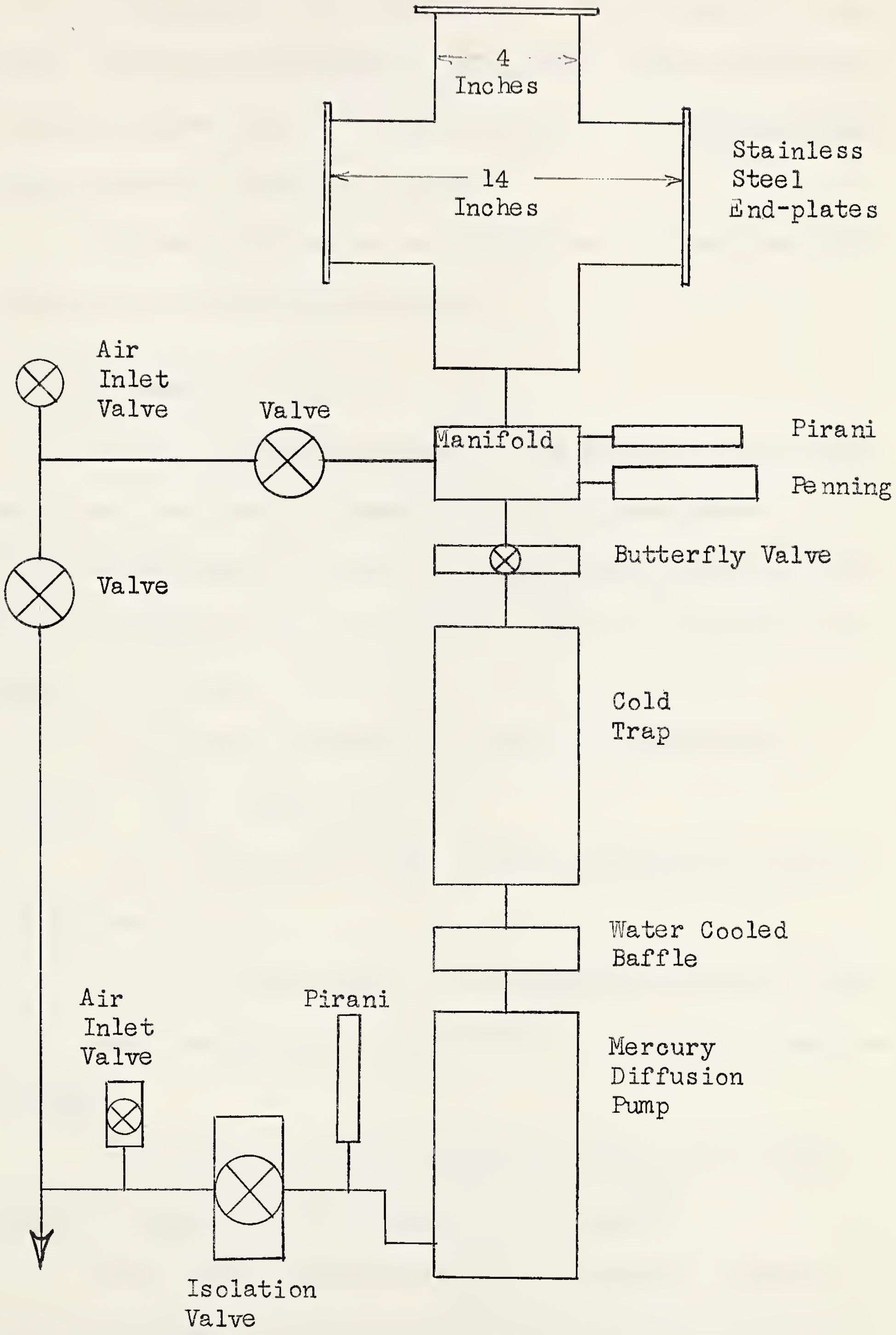

Figure 3.1.1 Vacuum System

was drawn. This was set to trip at about 3 ma. Since the breakdown current was much larger than this value, the supply would shut down at breakdown. This relay system also operated a solenoid controlled bar that discharged the filtering capacitors through a limiting resistor.

All parts of the vacuum system that did not have voltage applied to them were grounded.

3.2 Experimental Procedure

In the experiments performed the titania samples used were discs one inch in diameter and 0.1 inches thick. In the titania-vacuum gap series of experiments, the discs were fixed to either the top electrode or the bottom electrode by means of an adhesive material.

An adhesive material with special properties was desired. Some of these were:

(1) conductive so that no high voltage would develop across the adhesive.

(2) heat resistance - it was expected that the sample would reach temperatures of about 400° C if thermal breakdown occurred.

(3) soluble - it was necessary to remove the sample from the electrode after breakdown had occurred.

The adhesive material that was chosen was "Melton's Silver Solution". Other materials were considered but the

silver solution was the one that met the above specifications.

The electrodes were made to a Bruce profile(12) to ensure a uniform field through the center of the dielectric sample. The electrodes were about one inch in diameter and made of aluminum.

Current readings were made using a d-c pico-ammeter (Hewlett - Packard 425A). At all times except when readings were being made, this meter was kept shorted to prevent damage from current surges.

In all tests, the pressure was never above $5 * 10^{-6}$ and was usually about $1 * 10^{-6}$ mm Hg. Before each test the electrodes and sample were cleaned using toluene and acetone.

The applied voltage had to be raised slowly to prevent a filter capacitance charging current in excess of 3 ma which would shut down the power supply.

No current readings were made until at least 10 seconds had elapsed after a voltage was set. This time was allowed to permit the charging current to become negligible. The time constant of the capacitive charging current was set by the internal resistance and capacitance of the power supply and was calculated to be about 25 milliseconds. Thus 10 seconds was considered to be sufficient time for the capacitance charging current to become negligible.

3.3 Voltage - Current Relationships

(a) Titania

In this part of the investigation, the sample of titania was fixed between the two electrodes and current and temperature readings were taken for different fixed voltages. The temperature readings were made using a thermocouple fixed to the lower electrode. This was done to prevent field distortion.

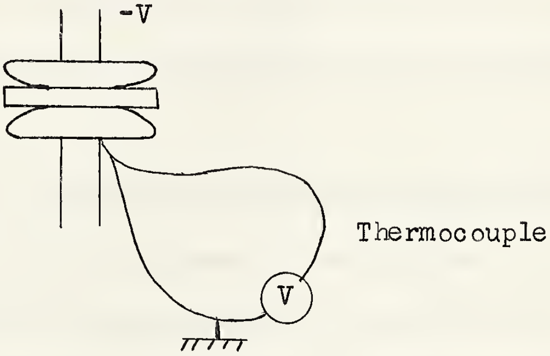

Figure 3.3.1 Electrode arrangement for the breakdown of titania

For low voltages (less than 3 kv), the current decreased with time reaching a constant value after about 30 minutes. When voltages above this were held constant, the current increased with time. Between 3 and about 13 kv it stopped rising after a length of time that increased with voltage. The temperature of the sample also rose to some constant

value in the upper part of this range (voltages greater than 10 kv). The steady state voltage-current relations for these ranges may be seen in figure 3.3.2. For voltages greater than 13 kv, both temperature and current rose for constant voltages. The relationship between temperature and current may be seen on figure 3.3.3. The rate at which they increased depended on the voltage applied (figure 3.3.4). Breakdown occurred in these tests. A path of dark material was formed through the sample which destroyed its insulating properties.

The decrease of current with time in the lower voltage region may be explained by the absorption current phenomena (section 2.1).

The increase of current for constant voltages between 3 and 10 kv with no noticeable change in temperature could be attributed to localized heating along some path where the non-homogeneity of the ceramic resulted in a greater than normal conductivity. Equilibrium would be reached when the heat leaving these paths was equal to the heat from resistive losses. The fact that a temperature change was not noted could be due to the poor heat conductivity of titania and the distance of the thermocouple from the sample. The noticeable temperature change between 10 and 13 kv would be due to the larger amounts of heat resulting from increased resistive losses.

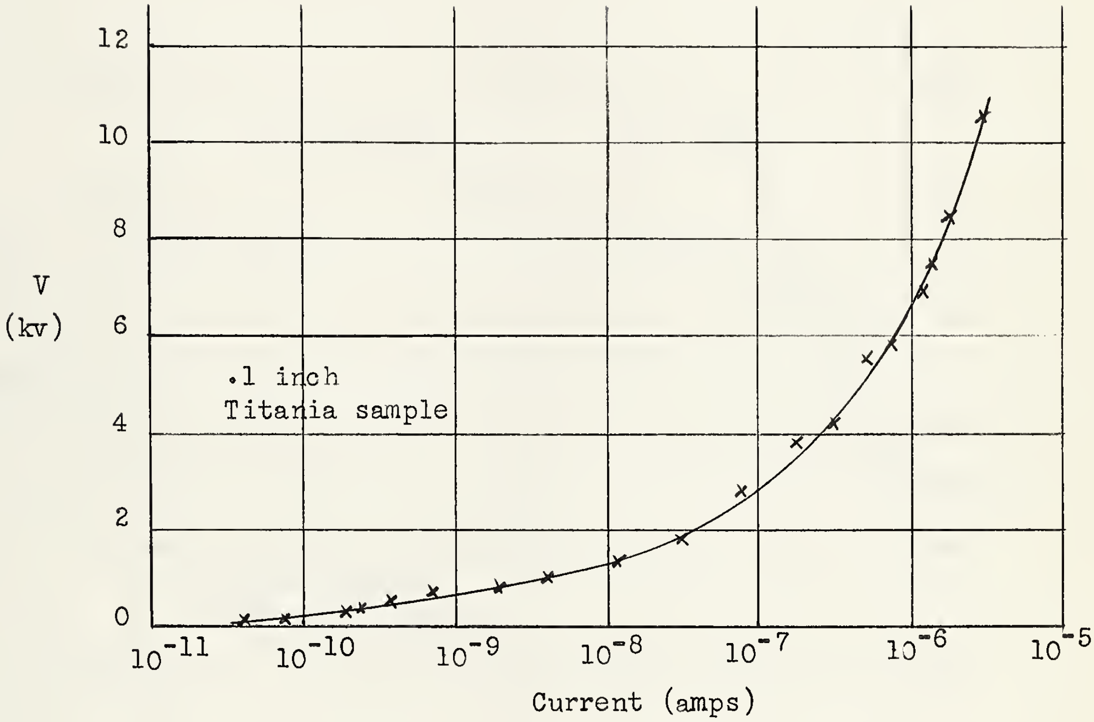

Figure 3.3.2 Voltage-current Characteristics of Titania

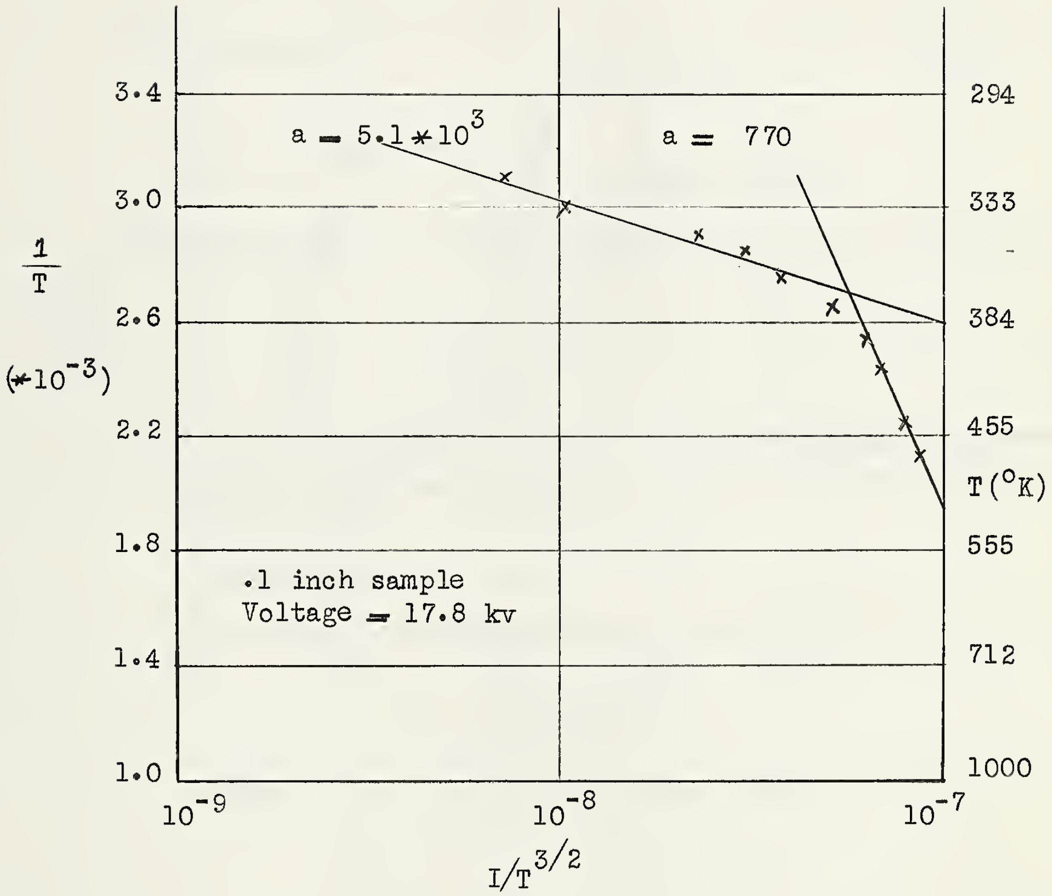

Figure 3.3.3 Temperature Dependence of $I/T^{3/2}$ for Titania

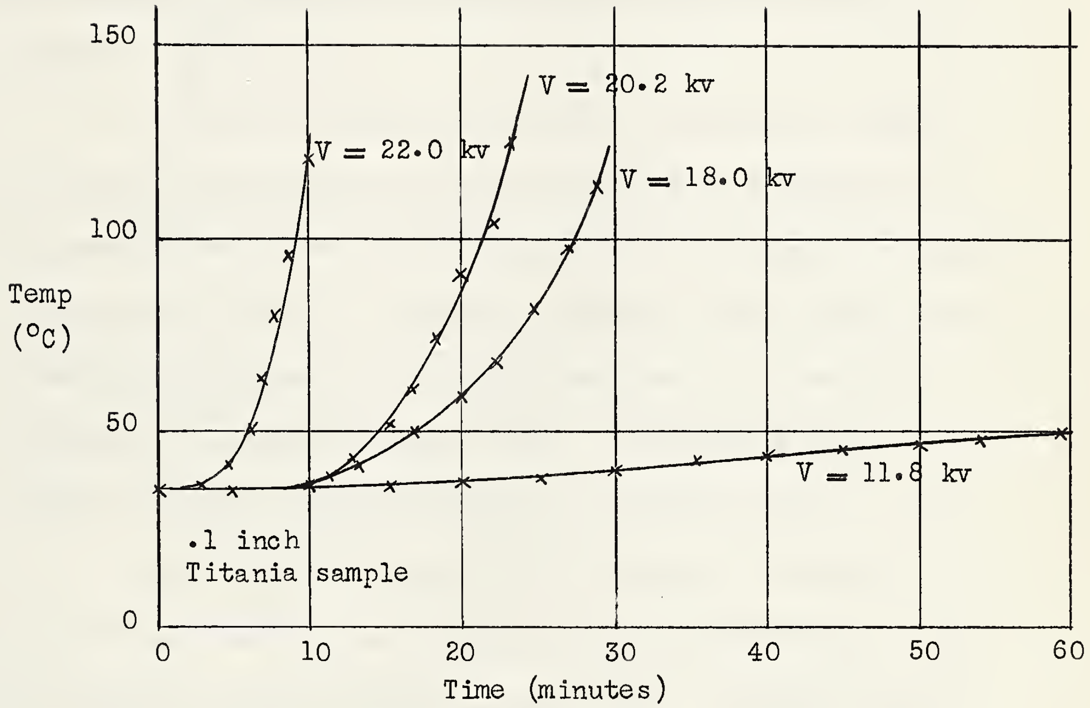

Figure 3.3.4 Temperature versus time for Titania

As can be seen from figure 3.3.3, the temperature dependence of current follows the type of relation predicted by equation 2.1.10 over a limited temperature range. The value of 'a' obtained from this curve is about 5×10^3. The theoretical value obtained in section 2.1 was about 2×10^4. The difference is probably due to a decrease in the energy gap width 'E_g' between the valence and conductance bands caused by impurities.

The change of slope in the higher temperature range of figure 3.3.3 may be due to the temperature dependence of the mobilities of the electrons and holes becoming significant. It may also be due to a partial reduction of the titania into a semiconducting material along paths where the localized temperature increase is quite high. This would yield a reduced value of 'E_g' resulting in a decreased value of 'a'.

A comparison of figures 2.2.2 and 3.3.4 indicates that thermal runaway has occurred in the titania sample when the applied voltage was above about 13 kv. The high temperatures resulting from this thermal runaway would cause the reduction of the titania to a semiconducting material which would carry the breakdown current. R Hayes(2) has shown that the particular type of titania used reduces to a semiconducting material at temperatures above 350°C in a vacuum. This temperature or higher was probably reached along some localized path since the temperature recorded before breakdown was always

above 200°C and usually approaching 400°C.

(b) Titania and a negative vacuum gap

In this part of the investigation, the sample of titania was fixed to the grounded electrode and a gap (.01 inches to .03 inches) was left between the top of the sample and the negative high voltage electrodes. Current and temperature readings were taken for various constant voltages.

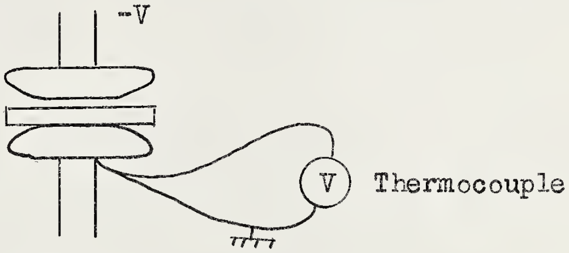

Figure 3.3.5 Electrode Arrangement for a Negative Gap

For low voltages, assuming no current was flowing, the field strength in the gap was given by

$$E_o = \frac{V}{d_o + \frac{d_1}{k}} \quad \text{v/cm} \qquad 3.3.1$$

where 'd_o' is the gap width, 'd_1' is the sample thickness, and 'k' is the dielectric constant of titania.

For small field strengths (less than about $5 * 10^4$ v/cm), the current was approximately zero. When the field strength was above this value, a measurable current flowed which decreased with time to some constant value. When the voltage was large enough so that the current was above $1 * 10^{-7}$ amps,

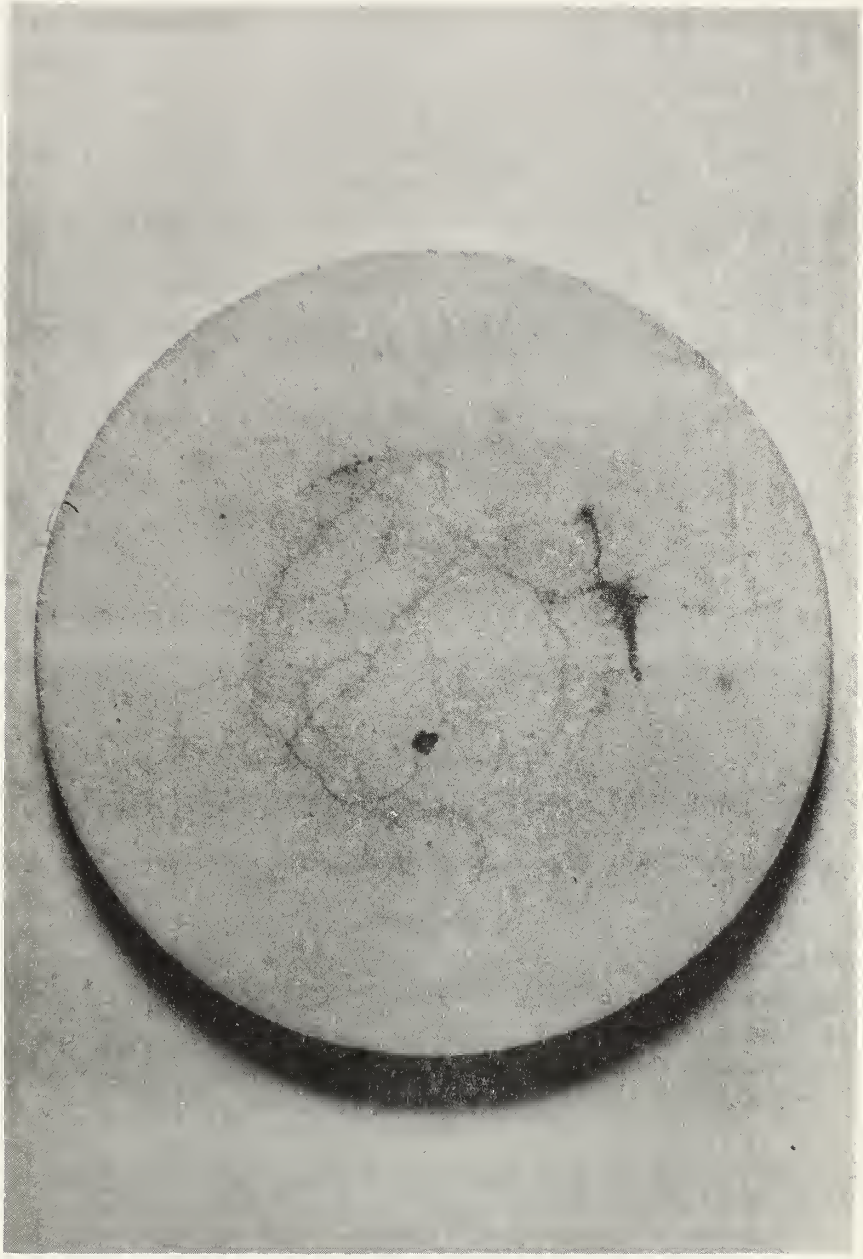

Figure 3.3.6 Negative Gap Sample

the current began to increase with time even though the voltage was held constant. When the current was greater than 1×10^{-6} amps, the temperature also began to increase. Breakdown occurred when the current had risen to some value above 5×10^{-5} amps in one case and 3×10^{-4} amps in another. The temperature recorded in both cases was above 350°C. The rate of temperature and current rise was dependent on the voltage across the electrodes. Breakdown in both cases took the form of a discolored path through the body of the discs with long tree-like branches (figure 3.3.6) on the surface facing the negative electrode. The branches were all linked with the point of breakdown on the surface. In one case, breakdown was violent enough to shatter the sample about the breakdown path.

The current that flowed for fields greater than about 5×10^{4} v/cm indicated that negatively charged particles were being emitted from the cathode. These particles collect on the surface of the ceramic and caused a potential which in turn causes a current to flow in the dielectric.

The fact that this current passed through the same stages as the current in the previous section, with about the same current boundaries, supports the theory that most of the voltage appears across the sample with only enough across the gap to provide the necessary emission current.

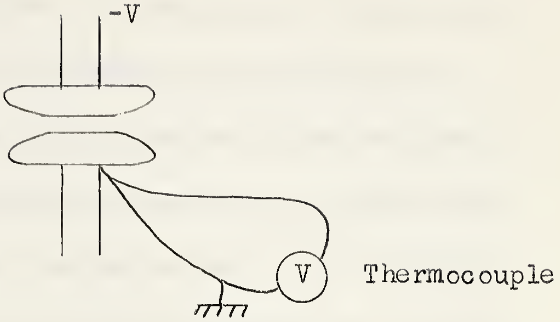

Figure 3.3.7 Electrode Arrangement for Emission

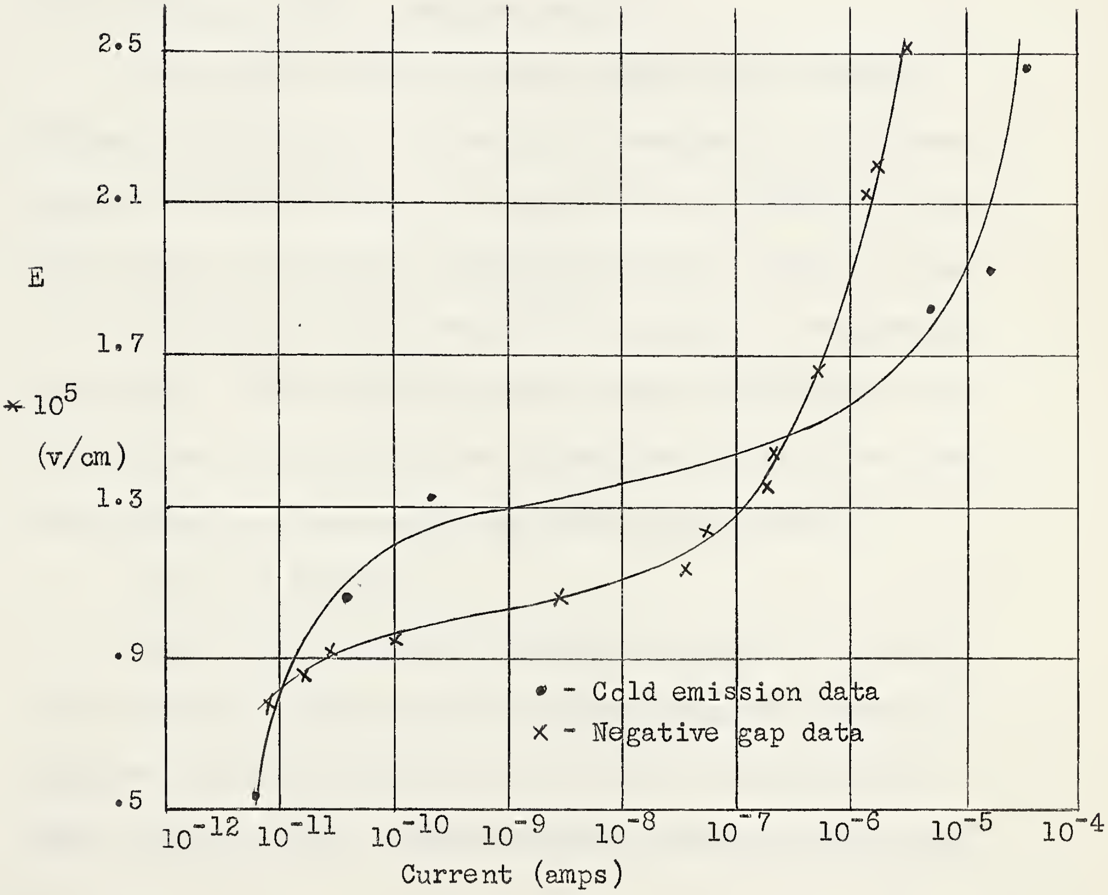

Figure 3.3.8 Cold Emission Characteristics

The resistive heating can lead to thermal instability (as in section 3.3.a) and raise the temperature sufficiently to cause the reduction of the titania along some path of localized heating. The tree-like branches on the surface of the sample may be due to electrons from areas of high charge concentration on the surface flowing to the point of breakdown. This flow would generate heat and reduce the titania along the path.

The sample that was shattered about the breakdown path probably broke due to thermal shock caused by the heat associated with the large breakdown current.

One sample, with lead borate glaze on the surface facing the vacuum gap, was taken to breakdown. No noticeable change in characteristics or improvement in breakdown strength was observed. The glaze (melting point about 480°C) appeared to have melted and flown away from the point of breakdown at the surface. This could have been caused by the escape of occluded gas from the titania through the melted glaze, and when exposed to the vacuum, the titania was reduced.

(c) Cold Emission

The electric gradient required to produce a current flow across the vacuum gap was studied using the aluminum electrodes used in the previous tests and a .029 inch gap width (figure 3.3.7). Current began to flow at about $5 * 10^4$

v/cm and reached a value of about $5 * 10^{-5}$ amps at a field strength of $2.7 * 10^{5}$ v/cm (see figure 3.3.8). The current flow was quite erratic. The temperature of the anode began to rise quite rapidly at field strengths above $1.6 * 10^{5}$ v/cm and was about 350°C at $2.7 * 10^{5}$ v/cm when the current was $5 * 10^{-5}$ amps.

The current flow across the vacuum gap is most likely due to field emission from the cathode. Field emission is very dependent on the finish of the emitting surface(13). Small projections on the surface can cause field enhancement resulting in currents at much lower values of field strength than predicted by the Fowler-Nordheim relations. These projections can break away from the cathode due to resistive heating and the strong fields, and this would cause the erratic currents that were recorded.

The current flow across the vacuum gap may have been partially due to ionic discharges in gas freed from the electrode and titania surfaces by resistive heating and bombardment heating(21). Since no appreciable pressure increase was recorded however, field emission from the cathode is probably responsible for all of the current flow.

The temperature increase undergone by the anode indicates that the impact of these high energy negative particles heats the bombarded surface. This would help to

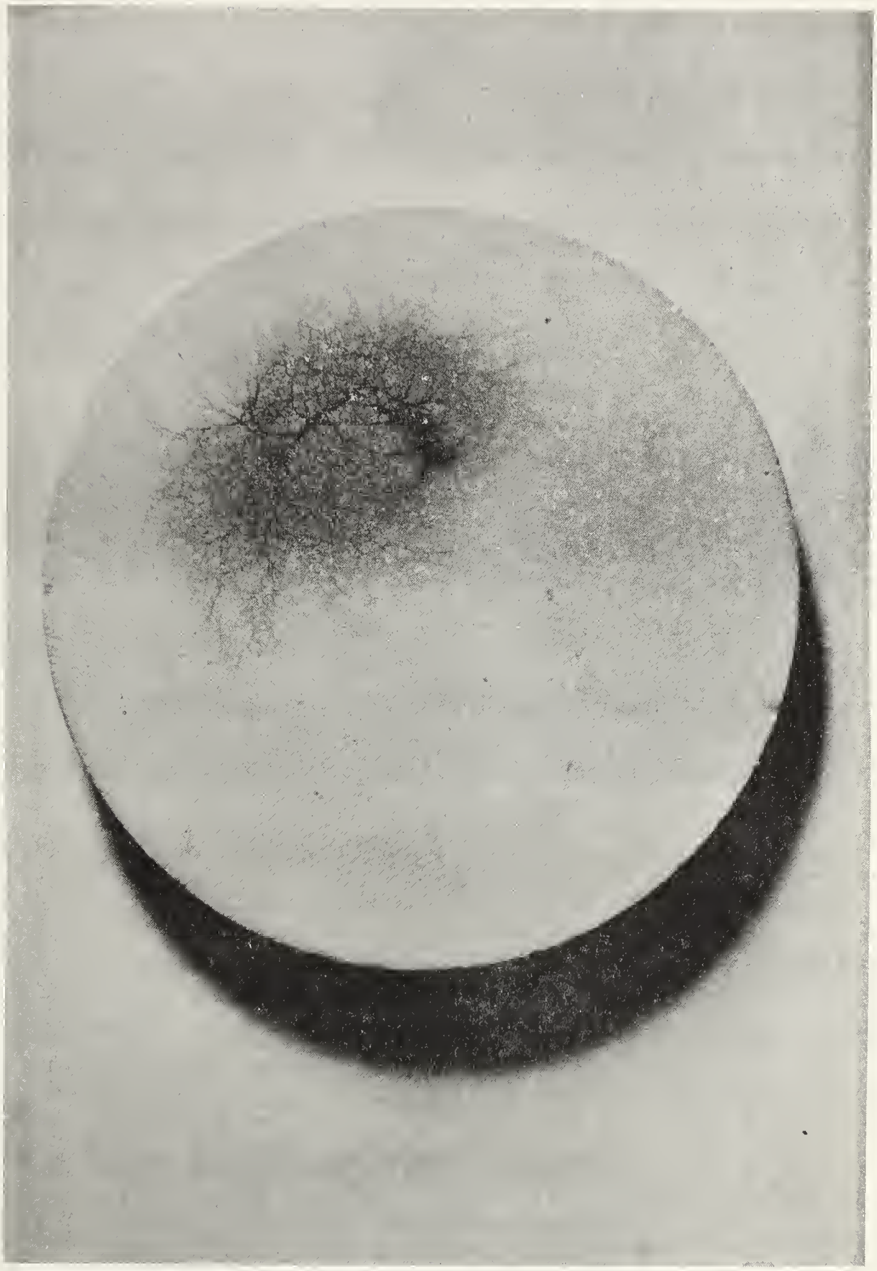

Figure 3.3.9 Positive Gap Sample

heat the surface of the titania in the previous section aiding the resistive heating process.

In addition to the emission current for various field strengths, figure 3.3.8 also has a curve showing the current flow that was obtained in the previous section for various gap field strengths. The field strengths were calculated using equation 3.3.2 which was obtained by assuming that no charge existed on the surface of the titania.

$$E = \frac{V}{d_0 + \frac{d_1}{k}} \qquad 3.3.2$$

From the two curves shown in figure 3.3.8, it may be seen that

(1) current begins to flow at approximately the same field strength in both cases, indicating that emission from the cathode is responsible for current flow.

(2) in the higher current range, the field strength necessary to emit a given current is less than the calculated field strength in the gap assuming no surface charging. This would indicate that charge has collected on the surface of the sample and decreased the gap voltage.

(d) Titania and a positive vacuum gap

In this part of the investigation, the sample was fixed to the negative upper electrode and a gap (.01 inches to .03 inches) was left between the bottom of the sample and the grounded

lower electrode. The temperature of the sample was not measured because of the difficulties of having the measuring apparatus at high voltages.

For small values of field strength (less than $1 * 10^5$ v/cm), the current was negligible. When the field strength was above $1 * 10^5$ v/cm, a current flowed which decreased to a constant value with time. When the voltage was large enough so that the current was above about $1 * 10^{-7}$ amps, the current began to increase with the voltage held constant. The rate at which the current increased depended on the voltage across the electrodes. Breakdown occurred when the current had risen to some value above $6 * 10^{-5}$ amps. After breakdown, a dark track existed through the body of the disc. The surface of the ceramic facing the gap had many fine tracks spread uniformly about the main breakdown path (figure 3.3.9).

The current that flows for fields greater than 10^5 v/cm suggests an emission current from the titania. Since no information could be found in the literature on insulator emission in strong electric fields, it is not possible to do more than postulate that it does occur from titania ceramics. The absorbed layers of gas on the surface of the titania may be partially responsible for the emission. Since experimentally, the field strength required for emission from the titania is about the same as for emission from the aluminum electrode, the surface of the titania may have metallic contam-

inants on it that are responsible for the emission.

Negative particles emitted from the titania would cause a negative charge deficit on the surface. This would result in a potential difference across the sample and current flow through it. The current flow would then exhibit the same qualities as the current in section 3.3.(b), i.e. the absorption current at low voltages and an increasing current with time at higher voltages with the change occurring when the voltage was large enough to produce a current of about $1*10^{-7}$ amps. The agreement of the actual results with these expected results support this explanation.

In sections 3.3.(a) and 3.3.(b) the current flowing just before breakdown was above $5*10^{-5}$ amps. In this section it was above $6*10^{-5}$ amps. Since the current is very temperature dependent, this suggests that the sample was at a high temperature when breakdown occurred.

The fine tracks on the surface of the disc are probably formed at breakdown when electrons from the breakdown path replace those removed by the emission process. Since the potential is large, this could produce enough additional heat to reduce the titania along these paths and produce the tracks.

3.4 Force across the vacuum gap

If a high voltage is applied to a series arrangement of titania and a vacuum gap, there is strong evidence (section 3.3.(b), 3.3.(c), and 3.3.(d)) that the titania supports a much larger voltage than that expected from theoretical considerations. When initially applied, most of the voltage exists across the vacuum gap due to the high dielectric constant of titania. This causes cathode emission and, by changing the amount of charge present at the surface of the titania, a redistribution of voltage. In order to measure the magnitude of this effect, the voltage at the surface of the titania disc is estimated by measuring the mechanical force across the vacuum gap.

(a) Negative gap

The force measurement is made in the vacuum chamber using the balance shown in figure 3.4.1.

The equation for the force across the vacuum gap is (from appendix II)

$$F = \frac{-\epsilon_o V^2 A}{{d_o}^2} (1 - a)^2 \text{ nts} \qquad 3.4.1$$

In this equation, 'V' is the applied voltage, 'd_o' is the width of the vacuum gap, 'A' is the effective area over which the force acts, and 'a' is the ratio of the voltage drop across the titania to the applied voltage ($0 \leq a \leq 1$). Variations in 'a'

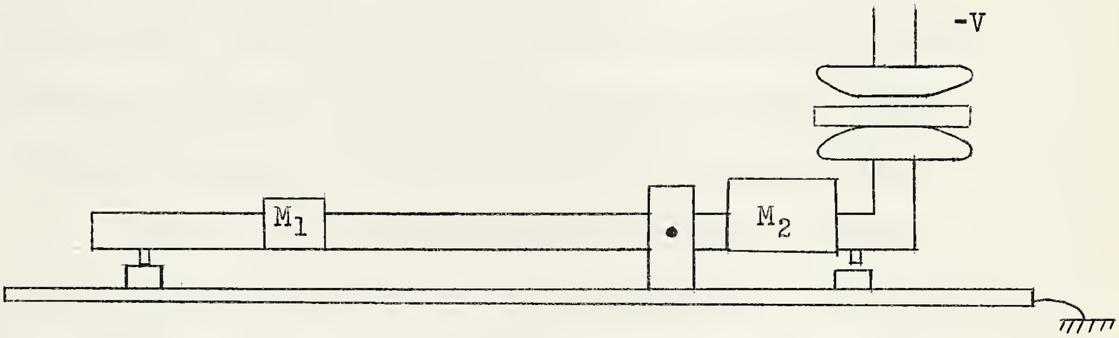

Figure 3.4.1 Balance for the Force Measurement (negative gap)

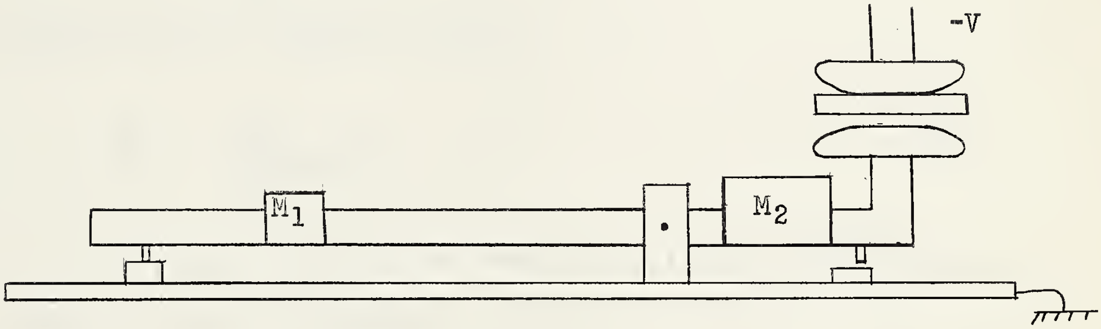

Figure 3.4.4 Balance for the Force Measurement (positive gap)

are due to charge collecting on the surface of the titania.

The width of the vacuum gap (d_o) that was used was .016 inches. When voltage was applied, the force across the vacuum gap was obtained by moving a mass (M_1 in figure 3.4.1) to the right until a point of equilibrium was encountered. This point was well defined since, when it was reached, the right hand side of the balance dropped. This increased d_o and thus decreased the force across the gap.

The force was measured for various applied voltages up to breakdown. A curve of V^2/F versus applied voltage is shown in figure 3.4.2. An examination of equation 3.4.1 indicates the reason for using this type of plot. Equation 3.4.1 is

$$F = \frac{-\epsilon_o V^2 A}{d_o^2} (1 - a)^2$$

Rearranging this equation yields

$$\frac{V^2}{F} = \frac{-d_o^2}{A\epsilon_o (1-a)^2} \qquad 3.4.2$$

Thus the variation of V^2/F with applied voltage for a fixed gap width is dependent upon 'a'.

Since, at low voltages, the field emission current is negligible, charging of the surface of the titania sample will not occur. Thus the voltage at the surface of the titania should be given by

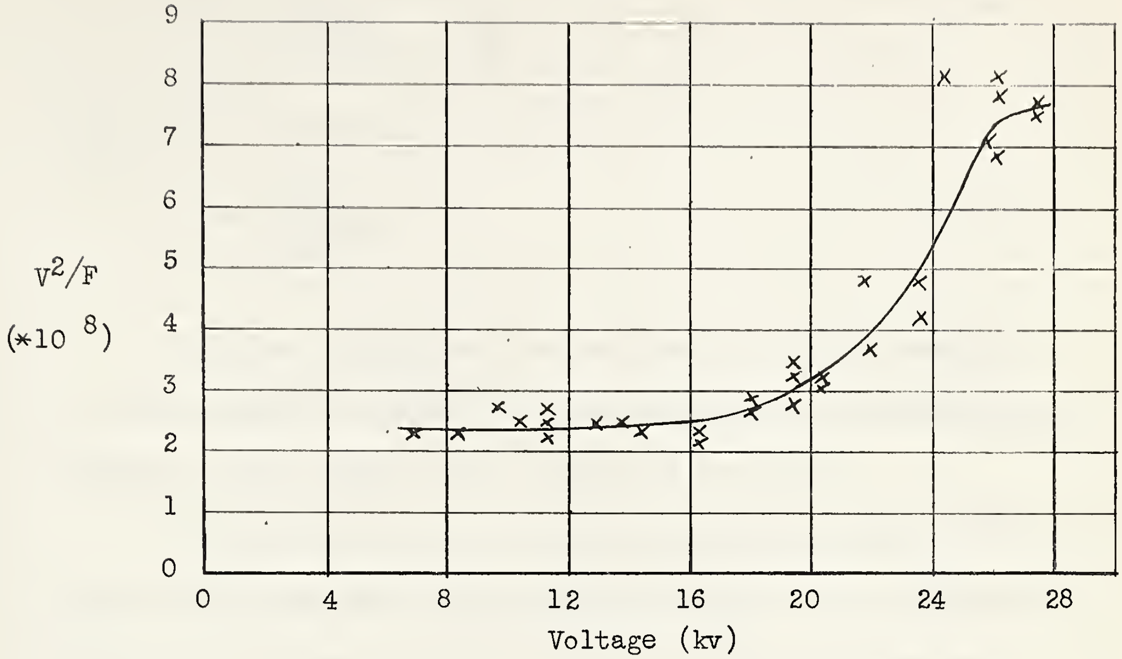

Figure 3.4.2 Variation of V^2/F with voltage (negative gap)

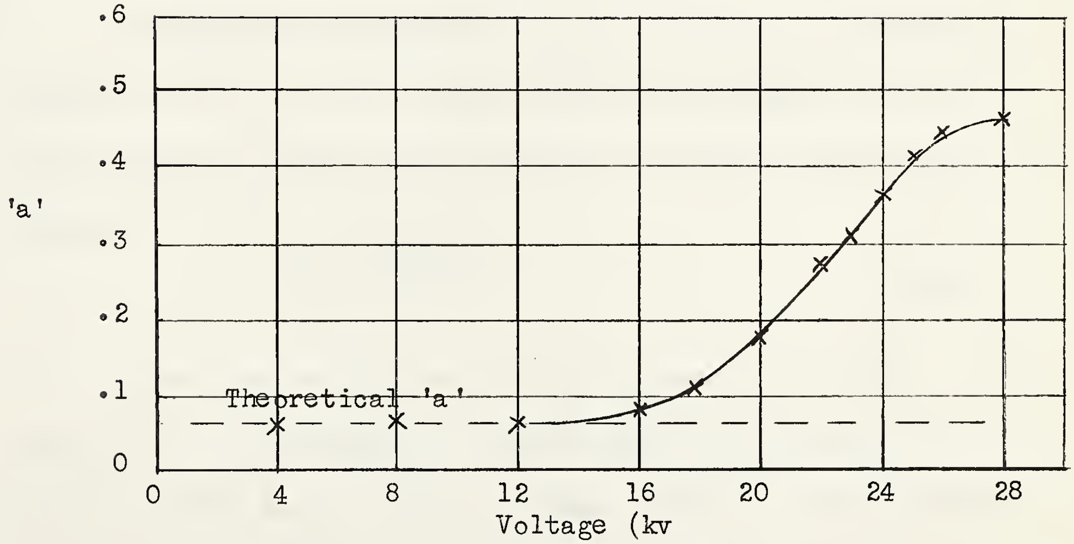

Figure 3.4.3 Fraction of the applied voltage across the titania for applied voltages up to breakdown (negative gap)

$$V_i = \frac{d_1}{kd_o + d_1} V \qquad 3.4.3$$

That is, 'a' should be

$$a = \frac{d_1}{kd_o + d_1} \qquad 3.4.4$$

With the arrangement that was used for this experiment, 'a' should have the value $a = .063$ (assuming that the dielectric constant of the titania (k) is 93) at low voltage.

Using this value of 'a' and the constant value of V^2/F from the low applied voltage region of figure 3.4.2, equation 3.4.1 may be solved for 'A' ('A' is the effective area over which the force acts). Solving this equation gives $A = .85$ cm^2. The value of 'A' that was expected due to the size and shape of the electrodes was about 1.2 cm^2.

The computed value of 'A' may then be used to calculate values of 'a' for larger values of applied voltage. If 'b' is the value of V^2/F given in figure 3.4.2, the solution of equation 3.4.2 for 'a' yields

$$a = 1 - \sqrt{2.2 \times 10^8/b} \qquad 3.4.5$$

A graph of 'a' versus applied voltage is shown in figure 3.4.3. The values of 'b' that are used in equation 3.4.5 to obtain figure 3.4.3 are taken from the 'average curve' on figure 3.4.2. It must be noted that the curve shown on

figure 3.4.3 is also an 'average curve'. Fluctuations that appear in figure 3.4.2 are probably due to changes of field strength in the vacuum gap caused by fluctuations in the cathode emission current.

As can be seen from figure 3.4.3, the fraction of the applied voltage across the titania sample was constant for low values of applied voltage. This indicates that the field strength was not great enough for cathode emission.

The fraction of the applied voltage that was across the titania sample increased at higher voltages, indicating that charge was collecting on the titania surface. This means that the field strength in the vacuum gap was large enough to cause an appreciable emission current to flow.

The levelling off of the curve in figure 3.4.3 at high voltages indicates that a greater fraction of the applied voltage is required to produce current flow across the vacuum gap than at lower voltages. This is perhaps due to the increased conductivity of the titania caused by resistive heating which means that less voltage is required to pass a given current through the titania sample.

Breakdown would follow when the temperature of the titania was great enough to reduce the titania to a semiconducting material. The high temperature would be due to thermal runaway which occurred when the voltage across the titania sample was great enough.

(b) Positive gap

The force measurement is made in the vacuum chamber using the balance shown in figure 3.4.4.

The equation for the force across the vacuum gap is (from appendix III)

$$F = \frac{\epsilon_0 V^2 A a^2}{d_0^2} \qquad 3.4.6$$

In this equation 'V' is the applied voltage, 'd_0' is the width of the vacuum gap, 'A' is the effective area over which the force acts, and 'a' is the ratio of the voltage drop across the vacuum gap to the applied voltage ($0 \leq a \leq 1$). Variations in 'a' are due to a deficit of charge at the surface of the titania. The fraction of the applied voltage that appears across the titania sample is '(1 - a)'.

The width of the vacuum gap that was used was .015 inches. When voltage was applied, the force on the electrode was obtained by moving a mass (M_1 in figure 3.4.4) to the right until a point of equilibrium was encountered. As in the previous section, this point was well defined.

Force measurements were made for different voltages up to breakdown. A curve of V^2/F versus applied voltage was obtained from the data and is shown in figure 3.4.5. As in the previous section, the reason for doing this is made clear by an examination of equation 3.4.6. That is

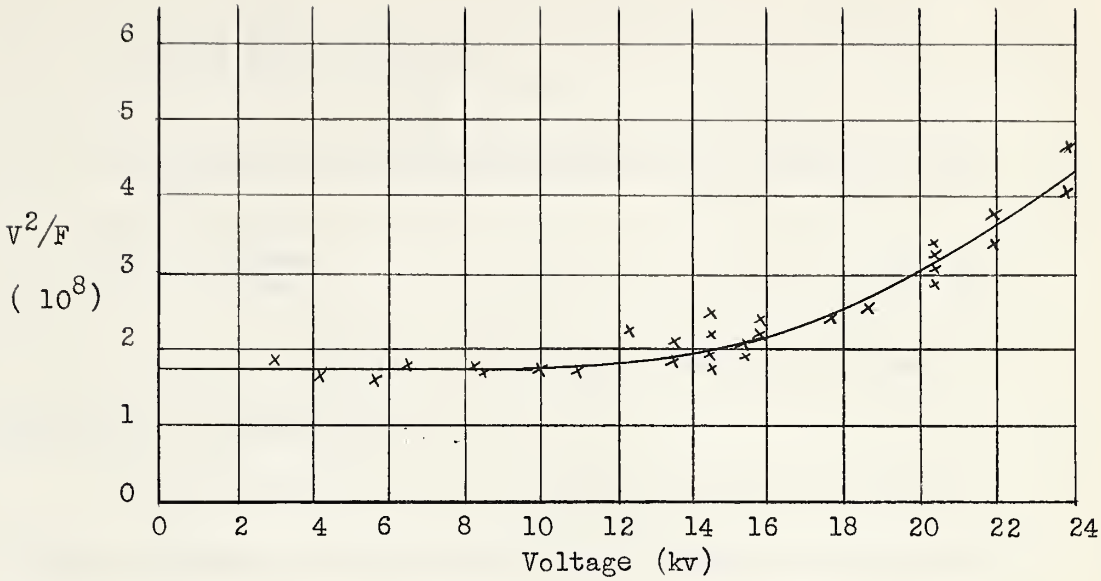

Figure 3.4.5 Variation of V^2/F with voltage (positive gap)

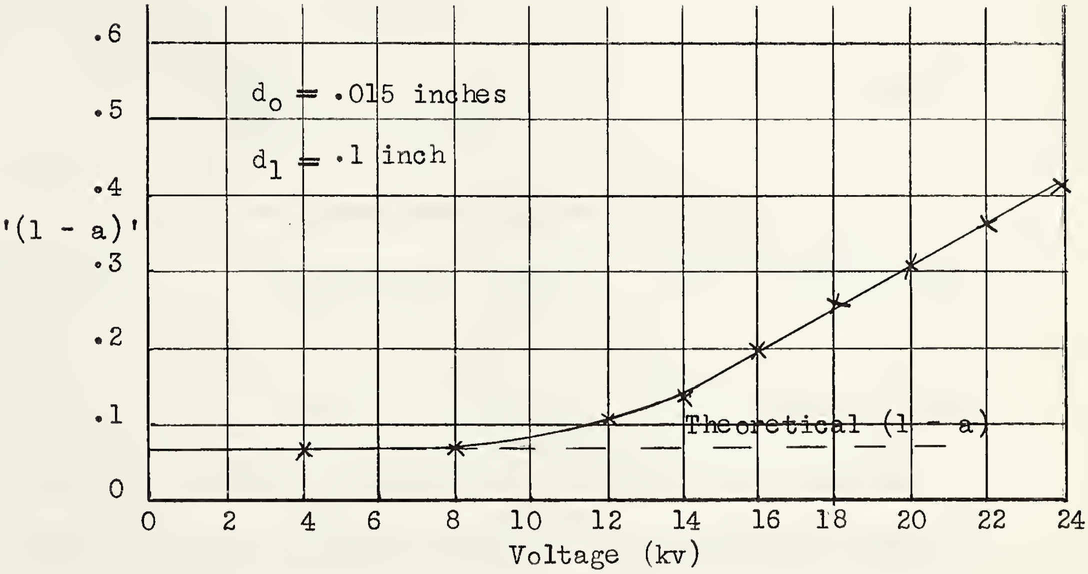

Figure 3.4.6 Fraction of the applied voltage across the titania for applied voltages up to breakdown (positive gap)

$$F = \frac{\epsilon_o V^2 A}{{d_o}^2} a^2 \text{ nts}$$

This equation may be rearranged and put into the form

$$\frac{V^2}{F} = \frac{{d_o}^2}{A \epsilon_o a^2} \qquad 3.4.7$$

Thus the variation of V^2/F with voltage for a fixed gap width is dependent upon 'a'.

At low voltages, where the emission current is negligible, charging of the surface of the titania will not occur. Thus the voltage at the surface of the titania should be given by

$$V_i = \frac{1}{1 + \frac{d_1}{d_o k}} V \qquad 3.4.8$$

That is, 'a' should be

$$a = \frac{1}{1 + \frac{d_1}{d_o k}} \qquad 3.4.9$$

With the electrode spacing that was used in this experiment, 'a' should take the value $a = .933$ (assuming that $k = 93$) for low values of applied voltage.

Using this value of 'a' and the value of V^2/F from the low voltage region of figure 3.4.5, equation 3.4.6 may be solved for 'A'. The value obtained for the effective area is $A = 1.08 \text{ cm}^2$. The difference is perhaps due to experimental error. Since the vacuum gap width was quite small and difficult

to measure accurately, and since 'A' depends on the gap width squared, most of the difference probably comes from errors in this measurement.

The computed value of 'A' that was obtained in this section may then be used to calculate the 'a' for larger values of applied voltage. If 'b' is the value of V^2/F from figure 3.4.5, 'a' as obtained from equation 3.4.7 is

$$a = \sqrt{1.52 * 10^8/b} \qquad 3.4.10$$

A curve of '(1 - a)' versus applied voltage is shown on figure 3.4.6. '(1 - a)' is used instead of 'a' because '(1 - a)' is the fraction of the applied voltage that appears across the titania sample.

As in the previous section, the 'b' from figure 3.4.5 used to obtain figure 3.4.6 are from an 'average curve'. Thus the curve on figure 3.4.6 is also an 'average curve'. Deviations from this curve are probably due to changes of field strength in the vacuum gap caused by fluctuations in the emission current.

As can be seen from figure 3.4.6, '(1 - a)' was constant at low values of applied voltage. This means that the field strength was not great enough for emission from the surface of the ceramic.

At higher voltages, the fraction of applied voltage that appeared across the titania sample increased (i.e. (1 - a) increased). This means that the emission currents were large

enough to cause an appreciable charge deficit at the titania surface.

When the voltage across the titania caused by this charge deficit was large enough, thermal runaway occurred and breakdown followed.

4. CONCLUSIONS

The punch through breakdown of titania and of titania and a vacuum gap in series was investigated.

A comparison of results obtained from Temperature - Time curves for various applied voltages with work done by Copple et al (14) indicated that thermal breakdown occurred in the titania sample. When the voltage exceeded some critical value, the heat losses in the ceramic were sufficient to raise the temperature to the point where chemical decomposition of the ceramic occurred. The temperature rise is a thermal runaway process due to the decrease of resistivity with temperature in the titania ceramic. At lower voltages, this same process occurs but insufficient power is available to cause a destructive temperature rise.

With titania and a vacuum gap in series, the breakdown process was modified by the vacuum gap. In the experiment with a negative vacuum gap, current flowed across the gap causing negative charge to accumulate on the surface of the titania. The current flow was probably due to field emission from the surface of the negative aluminum electrode. The field strength necessary for field emission was about two orders of magnitude less than the value expected from the Fowler-Nordheim relation. This was thought to have been due to field enhancement caused by small projections on the surface of the emitting

electrode. The charge that collected on the surface of the titania increased the voltage across the titania sample. When the voltage across the titania reached a sufficient size, thermal runaway occurred and this led to breakdown. In the investigations dealing with a positive gap, a similar process led to breakdown. A negative charge deficit developed at the surface of the titania causing an increase of voltage across the sample. When this voltage was large enough, high temperatures, resulting from thermal runaway, caused breakdown to occur. The charge deficit at the surface of the titania was thought to have been caused by negative charge emission from the surface of the titania. As in the case with a negative gap, this appears to be the only reasonable explanation for the current flow across the vacuum gap. Emission from the surface of the titania, caused by the strong electric fields in the vacuum gap, could be due to the effect of impurities or absorbed gas layers at the titania surface.

A thin coating of lead borate glaze was applied to the surface of the titania for one test in the negative gap part of the investigation. Since the glaze would prevent the exposure of the titania to the vacuum, it was thought that the reduction of titania to a semiconducting material would not occur. The glaze produced no appreciable change in the punch-through pre-breakdown or breakdown characteristics of

the titania. The glaze appeared to have melted and escaping occluded gas exposed the titania to the vacuum. It is possible that a glaze with a higher melting point would improve the punch-through breakdown strength of the titania.

The force measurement technique used in some of the investigations made in this thesis produced mainly qualitative results. This limitation was due mainly to fringe effects and to errors in gap width measurements. The limitation could be partially overcome if the metallic electrode was spherical. The field between a sphere and a plane can be calculated theoretically and this would eliminate much of the fringing field effect problem. The vacuum gap width could be measured quite accurately as only one point of contact would exist. If a small sphere and small gap widths were used, the emitting area would be very small and the point of breakdown on the surface of the sample could be chosen.

The method that was used to obtain the voltage across the titania sample by means of force measurements could be used in other investigations. Work has been done on the use of a dielectric coating on electrodes to improve their electrical breakdown strength in a vacuum(19). A modification of this force measurement technique could be used to further the investigation. Another possible use for this technique would be the investigation of emission from insulators.

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APPENDIX I

The theoretical temperature dependence of conductance for titania given by equation 2.1.10 is

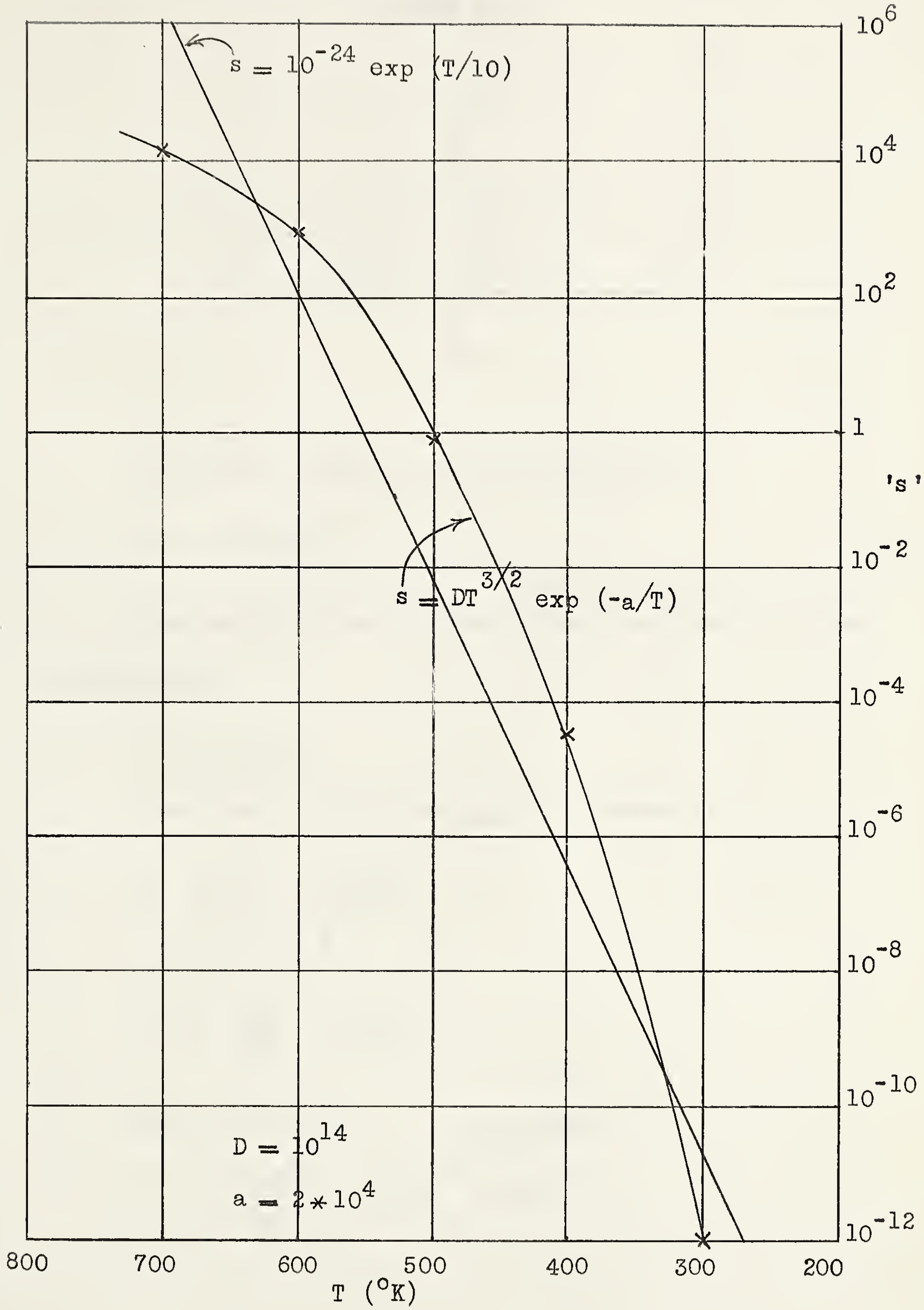
$$s = D\,T^{3/2} \exp(-a/T) \qquad 2.1.10$$

In this equation, the approximate value of the constants are $a \approx 10^4$ (section 2.1) and $D \approx 10^{14}$. The constant 'D' is obtained from the conductivity at room temperature which is about 10^{-12} ohm-cm (section 2.1).

The temperature dependence of conductivity used by Copple et al (14) for an insulator was

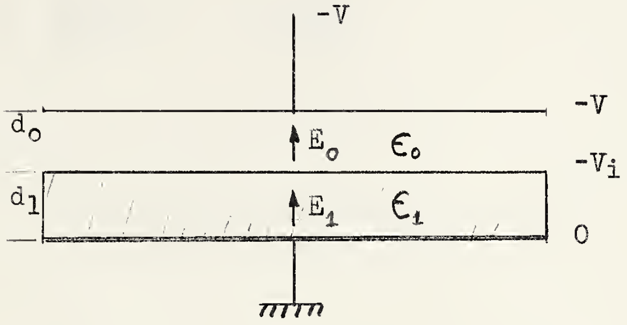
$$s = s_0 \exp(bT) \qquad 2.2.4$$

As can be seen from the graph on the following page, values of 's_0' and 'b' may be chosen so that equation 2.2.4 follows equation 2.1.10 approximately over the temperature range shown.



Theoretical Temperature Dependence of Conductivity

APPENDIX II: FORCE ON AN ELECTRODE ACROSS A NEGATIVE VACUUM GAP



The field strength in the vacuum gap is

$$E_o = \frac{V - V_i}{d_o}$$

The surface charge on the upper electrode is -g and is given by

$$-g = \epsilon_o E_o$$

Thus the force on the upper electrode is

$$F = g E_o \quad \text{nts/m}^2$$

$$F = -\epsilon_o E_o^2$$

$$F = \frac{-\epsilon_o}{d_o^2} (V - V_i)^2$$

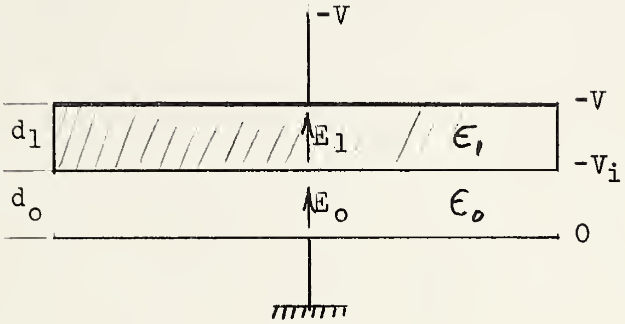
Let $V_i = aV \qquad (0 \leq a \leq 1)$

$$F = \frac{-\epsilon_o V^2}{d_o^2} (1 - a)^2 \text{ nts/m}^2$$

If the effective area over which the force acts is 'A', the net force is

$$F = \frac{-\epsilon_o V^2 A}{{d_o}^2} (1 - a)^2 \text{ nts}$$

APPENDIX III: FORCE ON AN ELECTRODE ACROSS A POSITIVE VACUUM GAP



The field strength in the vacuum gap is

$$E_o = \frac{V_i}{d_o}$$

The charge on the lower electrode 'g' is given by

$$g = \epsilon_o E_o$$

The force acting this electrode is

$$F = g\,E_o \quad nts/m$$

$$F = \epsilon_o\,E_o^2$$

$$F = \frac{\epsilon_o}{d_o^2}\,V_i^2$$

Let $V_i = aV \qquad 0 \leq a \leq 1$

$$F = \frac{\epsilon_o}{d_o^2}\,V^2\,a^2 \quad nts/m^2$$

If the effective area over which the force acts is 'A', this becomes

$$F = \frac{\epsilon_o V^2 A}{d_o^2}\,a^2$$

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